

Unstable Growth and Coarsening in Molecular-Beam Epitaxy

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Abstract

The coarsening dynamics of three-dimensional islands on a growing film is discussed. It is assumed that the origin of the initial instability of a planar surface is the Ehrlich-Schwoebel step-edge barrier for adatom diffusion. Two mechanisms of coarsening are identified: (i) surface diffusion driven by an uneven distribution of bonding energies, and (ii) mound coalescence driven by random deposition. Semi-quantitative estimates of the coarsening time are given in each case. When the surface slope saturates, an asymptotic dynamical exponent $z = 4$ is obtained.

1 Introduction

Nanometer-scale structures have been at the forefront of materials-related physics research for quite some time by now. This development is not only driven by the intriguing electronic and optical properties exhibited by these systems at reduced dimensions, but also by the arrival of modern surface characterisation techniques which enable one to monitor the *in situ* growth and to perform morphological and structural analysis down to atomic dimension on a routine basis. The vast amount of experimental research in this area offers ample opportunity for theoretical work in terms of materials modelling, simulation, and analysis.

One particular topic, which is the focus of this article, is the appearance of nanometer to micrometer scale surface modulations/islands in vapor-phase epitaxy. This phenomenon is usually regarded as the result of a growth instability, where a planar growth front (as in the layer-by-layer growth mode) becomes unstable. From a technological point of view, the instability is often undesirable in the fabrication of quantum heterostructures (such as semiconductor superlattices), although suggestions have been made to utilise the instability to grow nano-scale quantum dots[1].

In many epitaxial systems, a slight lattice mismatch (a few percent) is present between the substrate and the film, usually made of a different kind of substance. The strain energy builds up as the film grows thicker, and this can be the origin of a growth instability. In fact, it has been found that the strain in the film can relax in at least two different ways, (i) by misfit dislocations parallel to the film surface, and (ii) by surface rippling and “coherent” islanding. Detailed calculations have been performed to show that the gain in strain energy is enough to overcome either the dislocation energy or the capillary energy associated with surface ripples when the film becomes sufficiently thick. The kinetics of the relaxation process, sometimes involving an energy barrier, is a topic of current interest.

There is a second mechanism for unstable growth which can operate even in homoepitaxy. This was first pointed out by Villain[2] in 1991 and is due to a kinetic effect discovered by Ehrlich and Schwoebel [ES][3]. As seen from Fig. 1, the origin of the instability in this case is fairly obvious. At temperatures typical for vapor phase epitaxy (from room temperature to several hundred degrees centigrade) and especially for semiconductor films, the thermal energy $k_B T$ is much smaller than the barrier energy between neighboring surface sites. Hence adatoms move on the surface through thermally activated hopping, with a hopping rate given by the Arrhenius law

$$r \simeq \omega_D \exp(-E_B/k_B T), \quad (1)$$

where ω_D is the Debye frequency of the solid film. For some surfaces, the barrier energy E_B assumes a higher value at the step edge [Fig. 1(a)]. Due to the exponential dependence of r on E_B , a change of E_B by, say 0.5 eV can lead to a change of r by several orders of magnitude. Thus a higher barrier at the step edge (known as the ES barrier) can significantly reduce interlayer mass transport. During growth, adatoms are created at a constant rate by the beam. Although individual adatoms quickly thermalise with the substrate, the density of adatoms can be much higher than what it would be for an equilibrium surface. When the ES barrier is present, an asymmetry in the diffusion behaviour of adatoms around a step edge appears, as illustrated in Fig. 1(b). Adatoms which land on the upper terrace next to a step have nearly no access to the favorite bonding site at the step, while those on the lower terrace can diffuse freely to the bonding sites. A net current is thus created towards the step from the lower side. When a gentle surface slope is present, surface mass flow takes place in the direction of the slope. This flow is destabilizing for a high symmetry surface as an initially small fluctuation away from a flat surface is amplified by the up-hill current[2].

A number of kinetic Monte Carlo studies of solid-on-solid models of growth have been carried out. When the ES barrier is incorporated in the adatom hopping rates, three-dimensional surface modulations are indeed observed[4–

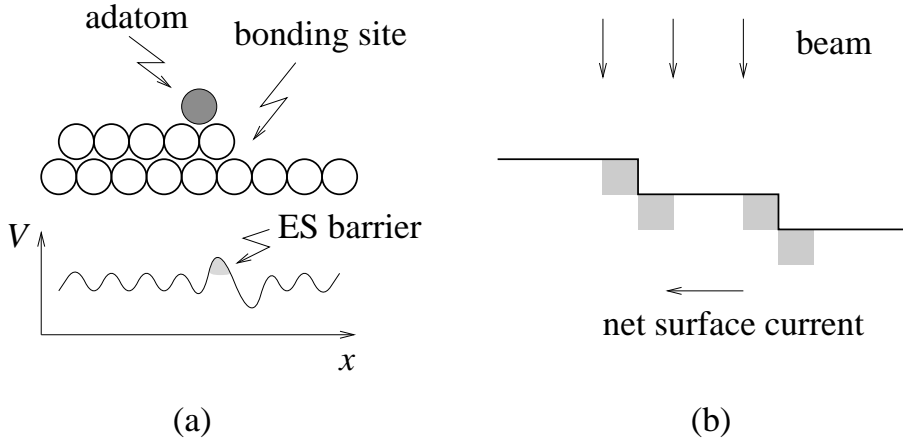


Fig. 1. (a) The Ehrlich-Schwoebel (ES) barrier prevents a thermalised adatom to jump down a step to reach the bonding site. (b) When a gentle surface slope is present, atoms arriving in the shaded area experience a diffusion bias due to the ES barrier: those landing on the lower side of a step are attracted by the step while those above are repelled. This asymmetry leads to a net surface diffusion current in the direction of the surface slope.

8]. The evolution of the surface modulation consists of two stages, analogous to the spinodal-decomposition phenomena in binary fluids and magnetic systems[9]. In the first stage, mounds with a characteristic lateral size grow rapidly in their height until their slope approaches a saturated value. This is known as the *initial transient regime*. (In some models, steepening continues to occur beyond the transient regime, but at a much slower rate.) In the second stage, the typical lateral size L of the mounds grows with continuing deposition. This phenomenon is known as *coarsening*. Both simulations and some experiments[5,10] have shown that the dependence of L on the film thickness H (see Fig. 2) can be fitted to a power-law

$$L \sim H^{1/z}. \quad (2)$$

The exponent $1/z$ generally lies in the range 0.15-0.25. The typical height of the mounds W can also be fitted to a power-law,

$$W \sim H^\beta, \quad (3)$$

where the exponent β can be as small as 0.25, or as big as 0.5.

The origin for the apparent nonuniversal value of the scaling exponents is unclear. This is in fact not surprising in view of the fact there is no clear picture why coarsening should take place in the first place. Due to this lack of understanding, there is quite a bit of uncertainty with regard to the way experimental or simulational data should be analysed. In the following we report some initial attempts in addressing these issues[11].

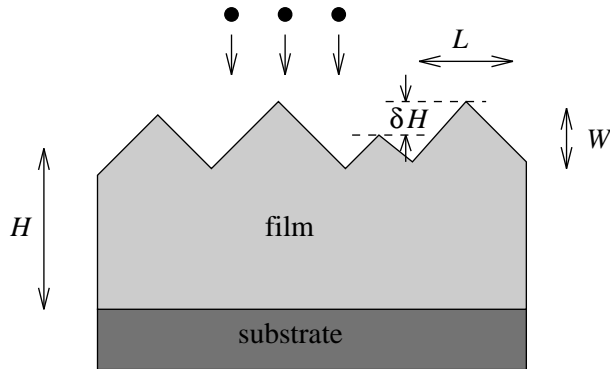


Fig. 2. Schematic illustration of the mound morphology during epitaxial growth. The typical mound size L increases with the film thickness H .

2 Bonding energy driven coarsening: relation to magnetic systems

Coarsening laws of the type (2) are quite familiar in statistical mechanics. In an Ising magnet, quenching a system from the high temperature disordered phase to below T_c , ordered domains form locally and then coarsen with time (see Fig. 3). The characteristic length L of the domain structure increases with time t as $L \sim t^{1/z}$. The value of the exponent z depends on whether the dynamics is conservative (e.g., as in Kawasaki spin exchange dynamics) or otherwise[9].

Several groups[12] have made the suggestion that, treating the gradient of the surface $\mathbf{m} = \nabla h$ as an order parameter, there is a direct analogy between the growth problem and the ordering dynamics of a planar magnet in two dimensions. So far, this analogy has been explored only formally and the similarities and differences between the two classes of problems have not been pursued in detail.

When the deposition noise in the growth problem can be ignored, there is indeed a close analogy between the growth problem and the Ising problem under conserved dynamics (Model B), though the coarsening exponent is different in two dimensions due to a difference in the transport mechanism operative. To see this, let us first review how the coarsening law in the Ising case under conserved dynamics is obtained. From Fig. 3, we see that the domain structure is fairly convoluted. The driving mechanism for coarsening is the surface tension associated with the domain walls. To reduce this excess free energy, spins need to diffuse around in such a way so as to eliminate points on the interface with the highest curvature. When the typical size of the pattern is L , the typical difference in chemical potential between favorable and unfavorable places along the interface is given by $\Delta\mu \sim L^{-1}$. At moderate temperatures and sufficiently large L , the dominant mechanism for transport is bulk diffusion, as anyone who has watched the evolution of the pattern on a computer

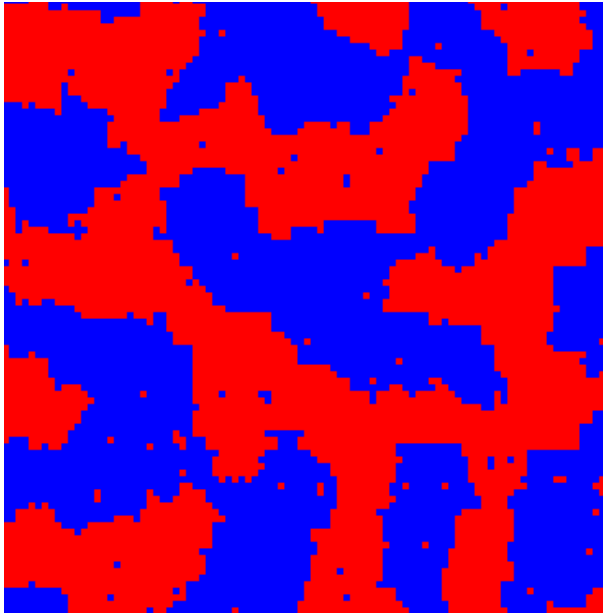


Fig. 3. Domain structure in an Ising model after quenching from the disordered phase to a temperature $T = 0.7T_c$. The simulation uses Kawasaki spin exchange dynamics. Note the isolated spins which diffuse through domains of opposite magnetisation. This bulk diffusion is responsible for the Lifshitz coarsening law $z = 3$.

can contest. Thus on average we expect a bulk current $j_B \sim \Delta\mu/L \sim L^{-2}$ across the domains and a rate of transport $r \simeq Lj_B \sim L^{-1}$ over an area L^2 . For the coarsening to take place, a finite fraction of spins in such an area need to diffuse through, yielding a coarsening time

$$\tau \simeq L^2/r \sim L^3. \quad (4)$$

This is the famous Lifshitz law.

Let us now see how the above picture can be modified to explain coarsening in the growth problem. For simplicity, let us first consider the mass transport between two neighboring mounds in a typical late-stage situation, as depicted in Fig. 4. The central part of each mound consists of roughly concentric rings of steps. The two mounds are joined by a “ridge terrace”. The outer rim of the ridge terrace has convex parts on either side and concave parts in the middle.

We assume that the newly deposited atoms are quickly captured by their nearby steps. These immediate bonding sites, however, may not be the energetically most favorable sites on the entire surface. This can be easily seen from Fig. 4, where sites on the convex parts of a step on average offer less lateral bonding than those on the concave parts. This is very similar to the surface tension effect in the domain coarsening problem discussed above. One can thus assign a chemical potential difference $\Delta\mu$ between the convex and

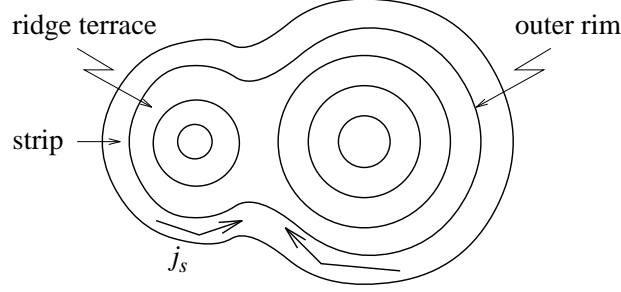


Fig. 4. Top view of two neighboring mounds of unequal size. Better lateral bonding for surface atoms is achieved at the concave parts of the closed steps. This mechanism results in an inward mass current j_s .

concave parts. Assuming the steps are locally thermal equilibrated, we have

$$\Delta\mu \simeq \gamma_s/L, \quad (5)$$

where γ_s is the step free energy per unit length, and L is the typical lateral scale in question (e.g., the distance between two centers).

Although the dependence of $\Delta\mu$ on L is the same as in the magnetic case, the transport mechanism here is different. This has to do with the geometry of the problem. As we have mentioned in the previous section, mounds are there because of the ES barrier, which suppresses interlayer transport. In order for an atom on the outer rim to reach the more favorable bonding sites at the center, it must diffuse either along the step, or on the terrace next to the step. In both cases, the diffusion is effectively one-dimensional as compared to the bulk diffusion in the Ising case. This gives rise to a slower coarsening law.

A semi-quantitative estimate of the coarsening time can now be obtained as follows. The average mass current on the ridge terrace due to the chemical potential difference (5) is given by,

$$j_s \simeq D_s \Delta\mu / L, \quad (6)$$

where D_s is a kinetic transport coefficient. (Note that D_s may depend on the mound slope when terrace diffusion dominates over ledge diffusion.) The same mechanism is expected to operate also in other layers below the ridge terrace, though j_s decreases due to the decreasing curvature of the steps. Let Q be the number of layers with significant inward mass transport, the total inward mass current is given by,

$$J_s \simeq Q j_s \simeq D_s \Delta\mu \frac{Q}{L}. \quad (7)$$

The process described above yields a gradual outward expansion of the neck

region connecting the two mounds. When the amount of mass M transported reaches a value comparable to the volume needed to fill in the gap, WL^2 , the two mounds coalesce. This leads to an estimate of the coarsening time,

$$\tau_b = M/J_s \simeq L^4 \frac{W}{\gamma_s D_s Q}. \quad (8)$$

With $Q \simeq W$, Eq. (8) yields $z = 4$.

3 Noise driven coarsening

Coarsening driven by an uneven distribution of bonding energies on the surface is effective only when the diffusion constant D_s is sufficiently large. Surface transport is strongly influenced by the substrate temperature. Thus, when the substrate temperature is low, coarsening due to this mechanism is extremely slow. In this section we discuss another coarsening mechanism: coarsening due to random fluctuations. Such a mechanism is present at all temperatures and it dominates when the previous mechanism is rendered ineffective by a low substrate temperature.

To illustrate how the noise mechanism works, let us consider a simple model where the inter-mound mass transport can be ignored completely. The height of each mound is now solely determined by the flux it receives from the beam. The total number N of atoms arriving within a surface area L^d when the film grows to a thickness H is $N \simeq HL^d/\Omega$. Here d is the dimension of the surface, and Ω the volume occupied by a single atom in the grown film. Due to the random nature of the vapor phase epitaxy, this number has a fluctuation

$$\delta N \simeq N^{1/2} \simeq H^{1/2} L^{d/2} \Omega^{-1/2}. \quad (9)$$

From the geometry illustrated in Fig. 2, we see that the height difference between neighboring mounds can not exceed significantly the typical height corrugation W of the mound array. This imposes a coarsening condition: the volume fluctuation $\Omega\delta N$ of a mound can not exceed the volume itself, WL^d . Equating the two terms, we obtain a coarsening time (measured in film thickness)

$$H \simeq W^2 L^d / \Omega. \quad (10)$$

In the regime where the power-laws (2) and (3) are well obeyed, Eq. (10)

yields,

$$\frac{2\beta}{d} + \frac{1}{z} = \frac{1}{d}. \quad (11)$$

If the mound slope $s \simeq W/L$ saturates to a constant, the above equation gives,

$$\beta = \frac{1}{z} = \frac{1}{d+2}. \quad (12)$$

A few comments on the coarsening laws derived here are in order. The noise mechanism does not explain why mounds form in the first place, nor does it tell us anything about the mound shape and slope. However, based on the assumption that there is an underlying mechanism for the formation of stable mounds, and that inter-mound transport is sufficiently slow, a relation between the geometrical parameters L, W and H characterising the mound array follows. This relation, of course, does not involve any of the microscopic details of the surface dynamics, provided the assumptions are met.

One might wonder why noise-fluctuation does not generate mound splitting. In simulation studies, mound splitting has indeed been observed, but it happens with a much smaller probability than the reverse process of mound coalescence. This obviously has to do with the assumed stability of individual mounds.

4 Which mechanism wins?

From Eq. (12), we see that the dynamical exponent z due to noise mechanism is equal to

$$z_n = 2 + d, \quad (13)$$

asymptotically at large L . If one takes the point of view that the bonding energy driven coarsening always invokes some sort of transport in $d - 1$ dimensions, then its corresponding dynamic exponent is given by

$$z_b = 4, \quad (14)$$

in all dimensions. Thus for $d < 2$ the noise mechanism dominates, while for $d > 2$ the bonding energy mechanism dominates, with $d = 2$ being the marginal case!

For $d = 2$, the bonding energy mechanism is expected to dominate at high substrate temperatures, while the noise mechanism should dominate at low

temperatures. A quantitative criterion can be constructed by comparing the timescales involved in each case. At a given deposition rate F , Eq. (10) yields a coarsening time $\tau_n = H/F = W^2 L^2 / (\Omega F)$ on scale L under the noise mechanism. Comparing it with τ_b given by (8), we obtain a dimensionless parameter

$$\alpha = \frac{\tau_b}{\tau_n} = \frac{\Omega F}{\gamma_s D_s s^2}, \quad (15)$$

where $s = W/L$ is the saturated slope of the mounds. The bonding energy mechanism dominates when $\alpha \ll 1$ ($\tau_b \ll \tau_n$), while the noise mechanism dominates when $\alpha \gg 1$ ($\tau_b \gg \tau_n$).

The next question is whether we can distinguish the two mechanisms based on a measurement of the surface profile. This turns out to be possible because the noise mechanism gives a specific relationship between the geometrical parameters H, W and L , all can be measured directly when we know the surface profile and film thickness. The quantities W and L can be defined precisely by examining the two-point correlation function[5]

$$G(\mathbf{x}, t) = \langle \tilde{h}(\mathbf{x}_0, t) \tilde{h}(\mathbf{x}_0 + \mathbf{x}, t) \rangle, \quad (16)$$

where $\tilde{h} = h - H$ is the fluctuation away from a flat film surface. We can identify the mound height W with the root-mean-square width of the corrugated surface,

$$W = \langle \tilde{h}^2 \rangle^{1/2} = G^{1/2}(0, t), \quad (17)$$

and the mound size L with the first zero of G , either along a given crystallographic direction or its radial average. (The function G typically has many oscillations for a mounded surface because of the anticorrelation of mound slopes over a distance L .) From the three geometrical quantities, we introduce a dimensionless parameter,

$$R = \frac{\Omega^{1/2} H^{1/2}}{W L^{d/2}}. \quad (18)$$

If coarsening is driven by noise, R should be of order 1. Otherwise, R should depend on the details of the surface dynamics, but its value should never exceed the limit set by the noise mechanism. (It is easy to see that R also measures the ratio between the excess material in a given mound due to fluctuations in the deposition rate, δN , and the total mound volume $W L^d$.)

An interesting property of (18) is that, for $d = 2$, $R = \text{const}$ implies $z = 4$ scaling of coarsening time when the mound slope $s = W/L$ saturates. Thus

the constancy of R can also be used as a test for the validity of such a scaling law. It should be noted that, even when this scaling does not hold, the value of R can still be used to distinguish between noise driven ($R \simeq 1$) and bonding energy driven ($R \ll 1$) coarsening.

In the real MBE experiment, both mechanisms are present and they play somewhat complementary role in the coarsening process. For example, the bonding energy mechanism is totally ineffective if we have a perfectly regular array of mounds. Symmetry then tells us that no mounds can grow at the expense of other mounds, and the whole pattern should stay put (although the shape of individual mounds may evolve). However, deposition noise will generate fluctuations in mound size and, coupled to the surface transport, eventually leads to coarsening. The surface transport is expected to become more significant during the final stage of a coalescence event, as there the curvature effects become greater, and the diffusion length becomes smaller. (If diffusion is totally ineffective, we would have the random deposition model with no mounds whatsoever. Thus the very existence of mounds demands some form of surface diffusion be present, though the diffusion may not be efficient enough to account for coarsening.)

Based on the above discussion, Tang, Smilauer and Vvedensky[11] proposed the following picture of mound coarsening: In the late-stage coarsening regime where mounds have acquired their quasi-stationary shape, deposition noise is responsible for generating the height difference (or equivalently, size disparity) between mounds through random fluctuations. Geometry sets a maximum $\delta H_m = W$ for the possible height difference. Bonding energy driven transport, on the other hand, speeds up the coarsening process by eliminating mounds which become too small compared to the rest. Effectively, it makes the surviving mounds more uniform in size. The quantitative importance of this effect depends on the parameter α .

5 Comparison with simulation and experimental results

The mound coarsening problem has been examined in quite a few numerical and experimental investigations, although a consensus on the coarsening law is yet to emerge. From the discussion reported above, it is seen that the coarsening time depends on a number of factors whose role can be different on different length scales and for different systems, experimental or otherwise. Therefore a careful assessment of the pattern and efficiency of surface mass transport, the importance of noise fluctuations, etc., is needed before a meaningful comparison of the values for z , often extracted from a limited range of data, can be made. This unfortunately has not been done for most of the experimental and simulational results that have been reported, making it diffi-

cult to test our theory. In the following we mention two exceptions: coarsening in $d = 1$, and a model studied by Smilauer and Vvedensky.

In the case $d = 1$, the noise driven coarsening picture is consistent with past simulation work, particularly the one by Kawakatsu and Munakata.[13] The model they studied can be interpreted in the surface growth context[12]. Numerical studies yields $z = 3$ which is consistent with (13).

In the second example, we mention a two-dimensional solid-on-solid model introduced by Smilauer and Vvedensky to model growth of both metal and semiconductor films with an ES barrier.[7]. The hopping rate of a surface atom follows the Arrhenius law (1), with the barrier energy E_B depending on the local bonding configuration, and the ES barrier when the move involves jumping down a step. Simulations were carried out at various temperatures for two sets of surface energy parameters.[7] In all cases examined, a mounded surface appears after an initial transient and the structure is observed to coarsen in time. In a recent work, Tang, Smilauer and Vvedensky computed the parameter R using the simulation data as a function of layer thickness H . They observed that, in all cases, R saturates to a constant value at late times, suggesting that the dynamic exponent z is indeed four. The actual asymptotic value of R depends on the surface temperature, being close to 1 at low temperatures, and much smaller than 1 at high temperatures. It is also found that the transition between the two regimes is fairly abrupt as the substrate temperature is increased, reflecting the exponential dependence of surface transport on temperature as suggested by the Arrhenius law. All these conclusions are consistent with the picture developed above.

To provide a more stringent test of the theory, future work should attempt to compute the step tension parameter γ_s and the diffusion constant D_s , either directly or in a numerical experiment with a suitable initial configuration of the surface. Much numerical work needs to be done in this direction.

6 Conclusions

The two mechanisms discussed in this paper, bonding energies and noise, all lead to coarsening of the mound array. Based on the pictures developed, quantitative estimates for the coarsening time are obtained. These estimates in particular allows one to derive asymptotic scaling laws when the mound slope saturates. In two dimensions, one obtains $z = 4$. It has been shown that these estimates are consistent with some existing simulational and experimental work. We believe the ideas and methods presented here offer a systematic way to analyse future simulational and experimental results.

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